(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) Publication number: **0 188 542 B1**

(12) EUROPEAN PATENT SPECIFICATION

(45) Date of publication of patent specification: **05.09.90**

(21) Application number: **85903589.1**

(22) Date of filing: **28.06.85**

(86) International application number:
PCT/US85/01256

(87) International publication number:
WO 86/00631 30.01.86 Gazette 86/03

(51) Int. Cl.^{5}: **C 08 L 77/06,** C 08 L 33/02,
C 08 K 5/09, C 08 K 5/13,
C 08 K 5/36

(54) BLENDS OF POLYAMIDES AND ETHYLENE POLYMERS CARBOXYLIC ACID GROUPS.

(30) Priority: **02.07.84 US 627327**

(43) Date of publication of application:
30.07.86 Bulletin 86/31

(45) Publication of the grant of the patent:
05.09.90 Bulletin 90/36

(84) Designated Contracting States:
BE DE FR GB IT NL SE

(56) References cited:
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US-A-3 620 878
US-A-4 105 709
US-A-4 310 638
US-A-4 346 196
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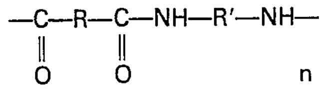
Courier Press, Leamington Spa, England.

Description

This pertains to improvements in compatibility and thermal stability of blends comprising polyamides and ethylene copolymers containing carboxyl functional groups by the addition to such blends of compatibilizing agents containing carboxylic groups.

Polyamides are well known commercial polymers wherein the structural units are linked by amide groupings —(CO—NH)— or —(CO—R—NH)—.

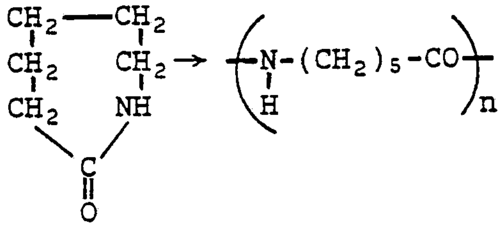
Some polyamides are known for their fiber-forming ability, such as those called by the sub-generic term "nylon" which are represented by the structure



$$-\underset{\substack{\| \\ O}}{C}-R-\underset{\substack{\| \\ O}}{C}-NH-R'-NH-\quad {}_{n}$$

where R and R′ represent, independently, one or more methylene groups and n is a plural number indicative of the molecular weight. These nylon resins are prepared by polymerizing a diamine with a diacid; nylons 6/6, 6/9, 6/10, and 6/12, e.g., belong in this classification.

Other nylons, e.g., nylons 6, 11 and 12 are prepared by polymerizing amino acids or amino acid derivatives. The highly commercialized nylon 6 is polymerized from the 6-carbon amino acid derivative, caprolactam:



Other polyamides, known as poly(amide-imide) are polymers based on reactions of tremellitic anhydride with aromatic diamines. While nylons are all polyamides, not all polyamides are nylons.

It is known that one may prepare blends of carboxyl-containing ethylene copolymers with polyamide resins to obtain such properties as high modulus, toughness, and elongation or to obtain superior adhesive properties for use in various hot melt adhesive and coating applications. See for example U.S. Patents 3,484,403; 4,018,733; 4,105,709; 4,132,690; and 4,478,978; U.K. Patent 2,052,528; and Belgian Patent 641,952. However, these blends are limited in utility due to their inherent thermal instability and incompatibility of each of the components. In a molten state (at typical compounding and applications temperatures of, e.g., $\geqq$149°C) the amine-functionality of the polyamide is free to react with pendant carboxyl groups on the polymer forming a crosslink. This results in gel formation and high viscosities, rendering the formulations useless.

It is known, for example, from U.S. Patent No. 4,346,196 to incorporate into such blends relatively low molecular weight compounds containing a carboxylic acid moiety, specifically stearic acid, as a lubricant and mould release agent.

The present invention provides a blend comprising at least one polyamide and at least one ethylene polymer containing carboxylic acid groups further characterized in that the blend also comprises from 1 to 10 parts per hundred (based on the total amount of the polyamide and the carboxylic acid-containing polymer) of at least one organic carboxylic acid compound having two, three or four carboxylic acid groups.

This invention differs from prior art in that it employs a compound having two, three or four carboxylic acid groups to considerably improve the stability of the formulation. This allows the development of new blends of polyamides and carboxyl-containing ethylene polymers that will have workable viscosities at application temperatures for several hours. This is ideal for systems where the formulation is kept in molten reservoirs prior to application. Even in melt-on-demand systems, voids can occur in the system, allowing stagnant hot melt to remain in the equipment and later be carried out with fresh material, causing contamination unless steps are taken to prevent interaction or gelation in the reservoir or else physically remove the residue. Extending the time period in which the material can be kept molten, without encountering appreciable deleterious effects, is sometimes referred to as "extending the pot-life".

This invention provides improvements in the thermal stability of polyamides when alloyed with carboxyl-containing functional polymers. This invention shows that a low molecular weight di-, or multi-functional acid (e.g. dicarboxylic acid) can be added to polyamide/carboxyl functional polymer blends and will reduce or prevent gelation. Preventing gelation means: first, that the polyamide/carboxyl function polymer blends are now more thermally stable; second, polyamides can now be alloyed with, and at a higher level of, carboxyl functional polymers than previously thought possible.

The ethylene/carboxyl containing copolymers used in the present invention are commercially available, especially those of the type known as "interpolymers", but may also be of the type known as "graft copolymers" and "block copolymers". These expressions are known to practitioners of the art. Interpolymers are made by polymerizing a mixture of the monomers; graft copolymers are made by grafting olefin acid groups onto a polyethylene chain; block copolymers are those wherein long polymer chains comprise chain segments of a polymerized plurality of ethylene units and segments of a polymerized plurality of the carboxyl-containing monomer units.

As used herein the expression "olefin acids" refers to olefinically-unsaturated carboxylic acids which are copolymerizable with ethylene, especially acrylic acid, methacrylic acid, crotonic acid, and 1-butenoic acid, most especially acrylic acid and methacrylic acid.

Patents which disclose interpolymerizations of ethylene and unsaturated carboxylic acids in a steady state reaction at high temperature and high pressure in a stirred reactor in the presence of a free-radical initiator are, e.g., Canadian Patent 655,298 (and its U.S. counterpart No. 4,351,931); U.S. 3,239,370; U.S. 3,520,861; U.S. 3,658,741; U.S. 3,884,857; U.S. 3,988,509; U.S. 4,248,990; and U.S. 4,252,924.

According to the present invention, the polyamides suitable for use as a starting material of the blend include any normally solid, substantially uncrosslinked polyamide which contains, as recurring groups, an amine nitrogen attached to a carbonyl. A convenient reference for further general information about nylons and polyamides is MODERN PLASTICS ENCYCLOPEDIA published recurringly by McGraw-Hill. The MERCK INDEX contains a limited amount of information about "nylon".

The typical polyamides of this invention are generally produced via the condensation reaction of diamines (ex. hexamethylene-diamine) and dibasic acids (e.g. adipic acids), or by polymerization of lactams (caprolactam) or amino acids. The resultant polyamides are either left amine-terminated or in some cases acid-terminated. When ethylene carboxyl containing polymers such as ethylene acrylic acid copolymers are admixed/alloyed with polyamides and subjected to high temperatures (i.e., about 149°C or more) the amide functionality of the polyamide will interact with the pendant carboxyl functionality of the carboxyl-functional polymer to yield severe crosslinking and gelation.

A similar problem also occurs with acid-terminated polyamides. Polyamides principally degrade via non-oxidative free-radical chain-scission which exposes the respective amine moiety. As with the example above, the carboxyl functional polymer can then easily react with the amine functionality of the polyamide.

In particular, the present invention relates to the inclusion of low molecular weight, low melting di, tri or tetra-functional organic acids (e.g. sebacic acid) to inhibit "interactive crosslinking" between the polyamide and the ethylene carboxyl-containing copolymer. Preferably the organic acid is based on an open-chain backbone.

"Thermal stability" is defined as being able to withstand elevated processing temperatures for an appreciable time without a significant change in viscosity or physical properties.

This problem of thermal instability is preferably alleviated by including low molecular weight dicarboxylic acids in the formulation to limit the reaction between the polyamides and the EAA copolymer. The dicarboxylic acid may correspond to the following formula: $HOOC(R)_xCOOH$ wherein R equals (CH_2), (CHOH) or (CH), or multiples or combinations of one or more of these, wherein x is an integer ranging from 1 to 14. Preferably (R) is an open-chain backbone and not cyclic.

Examples of di-carboxylic acids are: oxalic acid; malonic acid; succinic acid; glutonic acid; adipic acid; pimelic acid; suberic acid; azelaic acid; sebacic acid; dodecanedioic acid; 1,11-undecanedicarboxylic acid; hexadecanedioic acid; tartaric acid; and maleic acid.

Sebacic acid and tartaric acid are especially preferred.

Multi-carboxylic acids include those having 3 —COOH groups, such as citric acid, or those having 4 —COOH groups, such as pyromellitic acid or ethylene-diamine tetraacetic acid (EDTA), or low molecular weight oligomers of acrylic acid or methacrylic acid.

Good flowability and low viscosities are essential for successful hot melt and coating applications. Crosslinking or part gelation results in extremely high viscosity and poor flow characteristics. This invention provides thermal stability of polyamides (acid- and amine-terminated) and ethylene carboxyl-containing polymer alloys and, as a result of this invention, these alloys can produce commercially viable systems.

A unique and unexpected result of this invention is the ability to alloy ethylene carboxyl-containing polymers with polyamides (amine-terminated) that were previously impossible to alloy. The invention also allows alloying "higher levels" of ethylene carboxyl-containing polymers with polyamides (amine- and acid-terminated) before a compatibility problem is reached. This unique and unexpected ability allows new and useful alloys of polyamides and ethylene carboxyl-containing polymers for diverse property performance.

It is important for optimizing the success of this invention that both components (polyamides and ethylene carboxyl-containing polymers) be thermally stabilized themselves. As already mentioned, polyamides principally degrade via non-oxidative free-radical chain-scission which exposes the respective amine moiety. The ethenic portion of the ethylene carboxyl-containing polymers can degrade via oxidative and non-oxidative free radical crosslinking as well as chain-scission. The carboxyl portion, such as in the instance of ethylene/acrylic acid copolymers, tend to form intra- and inter-molecular anhydride crosslinks via a dehydration reaction when subjected to elevated temperatures. These anhydrides can also undergo a chain-scission, decarboxylation reaction at higher temperatures. Since the formation of free-radicals is intermediate to ultimate degradation of both polyamides and ethylene carboxyl-containing interpolymers, well-known free-radical scavengers (which are commonly sterically hindered phenolic stabilizers) are typically successfully used to impart improved thermal stability. However, the singular use of free-radical scavengers is ineffective for the blends of polyamides and carboxyl-containing ethylene polymer. Moreover, the mono-, di-, and multi-functional acids of the present invention are found to inhibit the particular anhydride crosslinking of the carboxyl portion of ethylene carboxyl-containing interpolymers. However, anhydride crosslinking does not appear to occur at ordinary hot melt application temperatures inasmuch as common free-radical scavengers can adequately stabilize the ethylene carboxyl-containing interpolymer singularly or independently.

While good flowability and low viscosities are essential for successful hot melt application, interactive crosslinking results in extremely high viscosities and poor flow characteristics at ordinary application temperatures (i.e. ≧149°C). This form of thermal instability is much different from the well-known forms/mechanisms by which polyamides and ethylene carboxyl-containing interpolymers degrade alone. Polyamides principally degrade via non-oxidative free-radical crosslinking as well as chain-scission.

As mentioned above the polyamide resins of the present invention are well-known thermoplastic condensation reaction products of one or more dibasic acid and one or more diamine. The reaction provides a generally linear molecular structure and relatively high molecular weights (i.e., generally between about 1,000 and 12,000). Present commercially available polyamide resins as well as those useful in the present invention exhibit Ring and Ball softening points generally between about 25° to about 200°C, and Brookfield viscosities generally between about 10—130 poise at 190°C but can be as little as about 1 to as much as about 500 poise at 190°C. The carboxyl-containing interpolymers of this invention include copolymers and terpolymers, where the carboxyl monomer(s) is an ethylenically unsaturated mono- or dicarboxylic acid and/or a vinyl ester of a C_1 to C_6 straight or branched chain aliphatic carboxylic acid. Examples of suitable carboxyl-containing polymers would include, but not be limited to, interpolymers of ethylene and acrylic acid, methacrylic acid, itaconic acid, maleic acid, fumaric acid, maleic anhydride, crotonic acid, or citraconic acid. Also suitable would be partially metal-neutralized ethylene interpolymers of acrylic acid and methacrylic acid. Blends of these various carboxyl-containing, ethylene interpolymers would also be considered to be within the purview of this invention. Preferably, interpolymers of ethylene with acrylic acid or methacrylic acid are used. As used herein, the expression "EAA" means an ethylene/acrylic acid copolymer; the expression "EMAA" means an ethylene/methacrylic acid copolymer.

Interactive crosslinking was found during oven-aging tests of amide functional polymer/ethylene acrylic acid copolymer blends. The interactive crosslinking took the form of complete gelling of the blend/formulation within 24 hours of oven-aging at 177—190°C. This gelation rendered the hot melt blend/formulation nonflowable and thus useless as a hot melt coating. Similar results occurred for two different 80/20 polyamide/ethylene acrylic acid copolymer blends where a single EAA resin was alloyed with two different polyamides. In laboratory trial applications utilizing a hot melt applicator at 190°C, severe gel formation and extremely high viscosities were observed within 2—4 hours and again the formulation became extremely viscous. Additional evaluations demonstrated that blends comprised of less than 15 wt. percent of an EAA resin (which itself consisted of about 20 wt. percent acrylic acid with a 15 melt flow at 125°C) were required to avoid appreciable gel formation in oven-aging tests at 190°C where the polyamide had a intermediate Ring and Ball softening point of approximately 110°C and a relatively low viscosity of 3.5 pascal seconds (Pa·s) or 35 poise at 190°C.

Where the polyamide had a fairly high Ring and Ball softening point of approximately 155°C and a fairly high Brookfield viscosity of 9.0—11.5 Pa·s (90—115 poise) at 190°C any and all blend proportions of about 20 weight percent acrylic acid ethylene copolymer caused severe gelling. This problem was solved by including low molecular weight dicarboxylic acids in the formulation according to the practice of the present invention to limit the reaction between polyamides and the EAA copolymer.

Other stabilizers which are effective free-radical scavengers, are recommended in addition to the dicarboxylic acids.

The following Tables illustrate the operable and preferred ranges of ingredients within the scope of this invention:

	Blend Composition	
Item	Operable	Preferred
ethylene/carboxyl-containing polymer	5—95% by wt.	10—30% by wt.
polyamide	5—95% by wt.	70—90% by wt.
carboxylic acid compatibilizer	1—10 pph	3—5 pph
free-radical scavenger	0—5 pph	0.5—1.0 pph

The term "pph" indicates parts per hundred parts of the polymer/polyamide blend and "% by wt." indicates percent by weight based on the polyamide and ethylene/carboxyl-containing polymer.

The properties of the ethylene/carboxyl-containing polymers within the scope of the present invention are as follows:

	Ranges	
Item	Operable	Preferred
carboxyl-containing comonomer, wt. %	3—34	14—25
melt flow value (MFV) in grams per 10 min. ASTM—D—1238(B)	1—500	10—150
melt flow value (MFV) in grams per 10 min. ASTM—D—1238(E)	20—10000	200—300
Brookfield Thermosel viscometer viscosity, in Pa·s (in poise)	1—1000 (10—10000)	10—400 (100—4000)

The properties of the polyamides within the purview of the present invention are:

	Ranges	
Item	Operable	Preferred
Viscosity in Pa·s (poise), as measured by a Brookfield viscometer, #3 spindle at 20 rpm	0.01—50	3—12
Ring and Ball softening pt., °C (ASTM E28—587)	25—220	100—190

The commercial and chemical identity of various exemplary free radical scavengers which may be used are as follows:

1. Mark 2047 (Witco Chemical), a phenolic-thioester stabilizer;
2. Irganox 1010 (Ciba Geigy), tetrakis(methylene 3,5-di-t-butyl-4-hydroxyphenol)) propionate methane;
3. Distearylthiodiproprionate (DSTDP) Witco Chemicals;
4. Santanox R (Monsanto) 4,4-thio bis(6-5-butyl m-cresol);
5. Topanol CA (I.C.I.) 3:1 condensate of 3-methyl-6-t-butyl phenol with crotonaldehyde;
6. Dilaurylthiodipropionate (DLTDP) Witco Chemicals.

The following experiments illustrate the advantages of the present invention. The following test conditions and units are used for the data here:

Item	Method
% AA or MAA in ethylene copolymer	ASTM—D4094
MVF (melt flow value) in grams per 10 min. (g/10 min.)	ASTM—D1238(B), except where noted
Oven aging-static test	samples left undisturbed in a forced air oven with an air circulation rate of approx. 0.18 meter^3/second (375 ft^3/min.)
Oven aging-color, gel formation, skinning	by visual inspection at recorded intervals
Viscosity Stability	Dynamic test-viscosity changes monitored using a Brookfield Thermosel viscometer (model RVTD, spindle 27, 20—50 Rpm) at 190°C; viscosity measured (CPS) at various times (T).

The following is provided as resin descriptions for the various resins used in the below experiments.

Polyamide-1 (P—1) an acid-terminated polyamide with a 105—115°C Ring and Ball softening point and 3—4 Pa·s (30—40 poise) Brookfield viscosity at 190°C.

Polyamide-2 (P—2) an acid-terminated polyamide with a 150—160°C Ring and Ball softening point and 9—11.5 Pa·s (90—115 poise) Brookfield viscosity at 190°C.

Polyamide-3 (P—3) an acid-terminated polyamide with a 160—170°C Ring and Ball softening point and 7—9 Pa·s (70—90 poise) Brookfield viscosity at 210°C.

Polyamide-4 (P—4) an amine-terminated polyamide with a 90—105°C Ring and Ball softening point and 3.5—5 Pa·s (35—50 poise) Brookfield viscosity at 210°C.

EAA—1 an ethylene acrylic acid copolymer with about 20 wt. percent acrylic acid and about 15 melt flow at 125°C, (ASTM D—1238B).

The blending of the components in these examples was done by melting them together in a vessel at 190°C, with stirring, using a forced-air oven, for about 0.5 to 1.0 hour. Other mixing means and devices may be employed, such as extrusion compounding.

Experiment 1 in Table A (not an example of the present invention) shows that when the carboxyl functional polymer (EAA—1) is blended with the acid-terminated polyamide, gelation occurred when the level of the carboxyl functional polymer was greater than fifteen percent (A to D). A flowable, non-gelling system was not obtainable when the carboxyl functional polymer was alloyed with an amine-terminated polyamide (E to H).

Experiments 2 and 3 (Table A) show that a more homogenous, compatible mixture which neither separates nor is altered by a chemical interaction is possible with the addition of a low molecular weight dicarboxylic acid (sebacic acid). The improved compatibility of the carboxyl functional polymer was possible when blending both the amine and acid terminated polyamide.

TABLE A - EAA/POLYAMIDE ALLOYS
(Forced Air Oven 190°C for 24 Hours)

	Alloy Components and Properties							
	A	B	C	D	E	F	G	H
Experiment 1*								
EAA-1 (wt. %)	15	25	50	85	15	25	50	85
P-4 acid terminated (wt. %)	--	--	--	--	85	75	50	15
P-1, amine terminated (wt. %)	85	75	50	15	--	--	--	--
Irganox 1010 (pph)	.5	.5	.5	.5	.5	.5	.5	.5
Compatibility**	C	G	G	G	G	G	G	G
Experiment 2								
EAA-1 (wt. %)	15	25	50	--	15	25	50	--
P-4 (wt. %)	85	75	50	--	85	75	50	--
Irganox 1010 (pph)	.5	.5	.5	--	.5	.5	.5	--
Sebacic Acid (pph)	5	5	5	--	10	10	10	--
Compatibility**	C	C	G	--	C	C	G	--
Experiment 3								
EAA-1 (wt. %)	15	25	50	--	15	25	50	--
P-1 (wt. %)	85	75	50	--	85	75	50	--
Irganox 1010 (pph)	.5	.5	.5	--	.5	.5	.5	--
Sebacic Acid (pph)	5	5	5	--	10	10	10	--
Compatibility**	C	C	G	--	C	C	G	--

* = Comparative experiment, not an example of the invention.

**C= Compatible, G = Gelled

Table B illustrates that as the level of dicarboxylic acid is reduced, the compatibility of the carboxyl-functional polymer with various types of polyamides is also reduced.

TABLE B

STABILIZED EAA BASED FORMULATION

Polyamide A		Polyamide B		EAA-1	Stabilizers		Results (190°C)	
Level wt. %	Type	Level wt. %	Type	Level wt. %	Level wt. %	Type	24 hrs*	40 hrs
57	P-1	19	P-2	19	5.0	Sebacic Acid	Flowable	Visc. but Flowable
63	P-1	19	P-4	19	5.0	Sebacic Acid	Flowable	- -
59	P-1	19	P2	19	3.0	Sebacic Acid	Flowable	Very Visc.
60	P-1	20	P-2	19	1.0	Sebacic Acid	Flowable	Gelled
74.5	P-1	- -	- -	20	5.0 0.5	Sebacic Acid Mark 2047	Flowable	Flowable
45	P-2	- -	- -	45	10	Sebacic Acid	Visc. but Flowable	Gelled
45	P-1	- -	- -	45	10	Sebacic Acid	0.5" Gelling of Surface	Gelled
45	P-4	- -	- -	45	10	Sebacic Acid	Gelled	- -

*All samples skinned within 24 hrs.

Table C shows that the thermal stability of polyamide (acid and amine-terminated)/carboxyl-functional polymer blends is significantly improved with the addition of the dicarboxylic acid. As the level of dicarboxylic acid is decreased so is the time interval before crosslinking starts or a significant increase in viscosity is noted.

TABLE C

VISCOSITY STABILITY OF COMPATIBILIZED BLENDS

Polyamide A		Polyamide B		EAA-1	Compatibilizers		Viscosity in Pa·s			
Level wt. %	Type	Level wt. %	Type	Level wt. %	Level wt. %	Type	0 (Hrs)	15 (hrs)	24 (hrs)	40 (hrs)
57	P-1	19	P-2	19	5	Sebacic Acid	3.250	1.150	1.525	9.000
63	P-1	19	P-4	19	5	Sebacic Acid	5.000	1.800		
59	P-1	19	P-2	19	3	Sebacic Acid	6.875	5.375	19.500	- -
60	P-1	20	P-2	19	1	Sebacic Acid	8.000	12.500	- -	- -
74.5	P-1	- -	- -	20	5	Sebacic Acid	3.750	1.850	- -	- -
					5	Mark 2047				

-- indicates that the value was not measured

To illustrate the effectiveness of this invention in coating applications each of the following specimen compositions were oven-aged and then coated onto Kraft paper and any problems with compatibility and thermal stability were observed (Table D). The components of the P—1/P—2/EAA—1 blends are in a 60/20/20 ratio, respectively.

TABLE D

Specimen*	2 Hours	4 Hours
1. P-1/P-2/EAA-1** 0 PPH Irganox 1010	very thick, gels, skinned	unpourable
2. P-1/P-2/EAA-1 0.5 PPH Irganox 1010	very thick, gels, skinned	bad skin, thick, bad gels
3. P-1/P-2/EAA-1 0 PPH Irganox 1010, 5 PPH Sebacic Acid	thin, skinned, no gels	thin, bad skinning, 2 gels
4. P-1/P-2/EAA-1 0.5 PPH Irganox 1010, 5 PPH Sebacic Acid	no gels, some skinning	no gels, some skinning
5. P-1/P-2/EAA-1 5 PPH Tartaric Acid 0.5 PPH Irganox 2047,	no skinning, no gels, unmelted tartaric acid	no skinning, 1 gel, unmelted tartaric acid

*PPH = parts per hundred of sample used

** = Comparative specimen, not an example of the present invention

The blend formulations of the present invention are useful as hot melt coatings on a wide variety of substrates, or as adhesive layers or bonding layers between a wide variety of substrates, such as metals, non-metals, glass, vitreous material, leather, paper, plastic, rubber, wood, and fabric. They are useful in bonding into a laminate, or other conglomerate structure, materials which are similar or dissimilar. They are especially useful for applications wherein they are applied to a first substrate, allowed to be cooled and stored, then subsequently heat-plasticized again to serve as an adhesive or bonding layer between the first substrate and a second substrate.

Claims

1. A blend comprising at least one polyamide and at least one ethylene polymer containing carboxylic acid groups further characterized in that the blend also comprises from 1 to 10 parts per hundred (based on the total amount of the polyamide and the carboxylic acid-containing polymer) of at least one organic carboxylic acid compound having two, three or four carboxylic acid groups.

2. A blend as claimed in Claim 1 wherein the said organic carboxylic acid compound is a compound of the formula $HOOC(R)_xCOOH$, wherein each R independently is CH, CH_2 or CHOH, and x is from 1 to 14.

3. A blend as claimed in Claim 2, wherein $(R)_x$ is an open chain non-cyclic backbone.

4. A blend as claimed in any one of Claims 1 to 3, wherein the said organic carboxylic acid compound is oxalic acid; malonic acid; succinic acid; glutonic acid; adipic acid; pimelic acid; suberic acid; azelaic acid; sebacic acid; dodecanedioic acid; 1,11-undecanedicarboxylic acid; hexadecanedioic acid; tartaric acid; or maleic acid.

5. A blend as claimed in Claim 4 wherein the said organic carboxylic acid compound is sebacic acid or tartaric acid.

6. A blend as claimed in Claim 1, wherein the said organic carboxylic acid compound is citric acid, pyromellitic acid, ethylenediamine tetraacetic acid, or a low molecular weight oligomer of acrylic acid or methacrylic acid, containing 3 or 4 COOH groups.

7. A blend as claimed in any one of the preceding claims wherein the ethylene polymer containing carboxylic acid groups is a random, homogeneous, interpolymer of ethylene and acrylic acid wherein the ethylene units comprise at least 65 percent by weight of the interpolymer.

8. A blend as claimed in any one of the preceding claims comprising 10 percent to 30 percent of at least one ethylene polymer containing carboxylic acid groups 70 percent to 90 percent of at least one polyamide, 3 percent to 5 percent of the said at least one organic carboxylic acid compound, and from 0.5 to 1 percent of a free-radical scavenger or antioxidant.

9. A process for improving the pot life of a blend of at least one polyamide and at least one ethylene polymer containing carboxylic acid groups, said method comprising incorporating into said blend an organic carboxylic acid compound as defined in any one of Claims 1 to 6.

Patentansprüche

1. Mischung enthaltend mindestens ein Polyamid und mindestens ein Carbonsäuregruppen enthaltendes Ethylenpolymer, weiterhin dadurch gekennzeichnet, daß die Mischung noch enthält 1 bis 10 Teile pro hundert (bezogen auf Gesamtmenge von Polyamid und Carbonsäuregruppen enthaltendem Polymer) mindestens einer organischen Carbonsäureverbindung mit zwei, drei oder vier Carbonsäuregruppen.

2. Mischung nach Anspruch 1, dadurch gekennzeichnet, daß die organische Carbonsäureverbindung eine Verbindung der Formel $HOOC(R)_xCOOH$ ist, in der jedes R unabhängig CH, CH_2 oder CHOH ist und x 1 bis 14 ist.

3. Mischung nach Anspruch 2, dadurch gekennzeichnet, daß $(R)_x$ ein offenkettiges, nicht zyklisches Rückrat ist.

4. Mischung nach jedem der Ansprüche 1 bis 3, dadurch gekennzeichnet, daß die organische Carbonsäureverbindung Oxalsäure, Malonsäure, Bernsteinsäure, Glutarsäure, Adipinsäure, Pimelinsäure, Korksäure, Azelainsäure, Sebacinsäure, Dodecandisäure, 1,11-Undecandicarbonsäure, Hexadecandisäure, Weinsäure oder Maleinsäure ist.

5. Mischung nach Anspruch 4, dadurch gekennzeichnet, daß die organische Carbonsäureverbindung Sebacinsäure oder Weinsäure ist.

6. Mischung nach Anspruch 1, dadurch gekennzeichnet, daß die organische Carbonsäureverbindung Zitronensäure, Pyromellitsäure, Ethylendiamintetraessigsäure oder ein Oligomer von Acrylsäure oder Methacrylsäure mit niedrigem Molekulargewicht ist, das 3 oder 4 COOH-Gruppen enthält.

7. Mischung nach jedem der vorstehenden Ansprüche, dadurch gekennzeichnet, daß das Carbonsäuregruppen enthaltende Ethylenpolymer ein statistisches, homogenes Mischpolymer von Ethylen- und Acrylsäure ist, wobei die Ethyleneinheiten mindestens 65 Gew.-% des Mischpolymeren enthalten.

8. Mischung nach jedem der vorstehenden Ansprüche, dadurch gekennzeichnet, daß sie enthält 10 bis 30% mindestens eines Carbonsäuregruppen enthaltenden Ethylenpolymers, 70 bis 90% mindestens eines

Polyamids, 3 bis 5% der mindestens einen organischen Carbonsäureverbindung und von 0,5 bis 1% eines Fängers für freie Radikale oder Antioxidants.

9. Verfahren zum Verbessern der Topfzeit einer Mischung aus mindestens einem Polyamid und mindestens einem Carbonsäuregruppen enthaltenden Ethylenpolymer, gekennzeichnet durch Einbringen in die Mischung einer organischen Carbonsäureverbindung gemäß jedem der Ansprüche 1 bis 6.

Revendications

1. Alliage comprenant au moins un polyamide et au moins un polymère d'éthylène contenant des groupes acides carboxyliques, caractérisé en plus par le fait que l'alliage comprend également de 1 à 10 parties pour cent (rapporté à la quantité totale du polyamide et du polymère contenant l'acide carboxylique) d'au moins un composé acide carboxylique organique ayant deux, trois ou quatre groupes acides carboxyliques.

2. Alliage, tel qu'il est revendiqué dans la revendication 1, dans lequel ledit composé acide carboxylique organique est un composé de formule $HOOC(R)_xCOOH$, dans laquelle R indépendamment est CH, CH_2 ou CHON et x est compris entre 1 et 14.

3. Alliage, tel qu'il est revendiqué dans la revendication 2, dans lequel $(R)_x$ est un squelette non cyclique à chaine ouverte.

4. Alliage, tel qu'il est revendiqué dans l'une quelconque des revendications 1 à 3, dans lequel ledit composé acide carboxylique organique est l'acide oxalique, l'acide malonique, l'acide succinique, l'acide glutarique, l'acide adipique, l'acide pimélique, l'acide subérique, l'acide azélaique, l'acide sébacique, l'acide dodécanedioïque, l'acide 1,11-undécanedicarboxylique, l'acide hexadécanedioïque, l'acide tartrique ou l'acide maléique.

5. Alliage, tel qu'il est revendiqué dans la revendication 4, dans lequel ledit composé acide carboxylique organique est l'acide sébacique ou l'acide tartrique.

6. Alliage, tel qu'il est revendiqué dans la revendication 1, dans lequel ledit composé acide carboxylique organique est l'acide citrique l'acide pyromellitique, l'acide éthylènediamine-tétraacétique, ou un oligomère à faible masse moléculaire d'acide acrylique ou methacrylique contenant 3 ou 4 groupes COOH.

7. Alliage, tel qu'il est revendiqué dans l'une quelconque des revendications précédentes, dans lequel le polymère d'éthylène contenant les groupes acides carboxyliques est un interpolymère statistique homogène d'éthylène et d'acide acrylique dans lequel les unités éthylène constituent au moins 65 pour cent en poids de l'interpolymère.

8. Alliage, tel qu'il est revendiqué dans l'une quelconque des revendications précédentes, comprenant 10% à 30% d'au moins un polymère d'éthylène contenant des groupes acides carboxyliques, 70% à 90% d'au moins un polyamide, 3% à 5% d'au moins un composé acide carboxylique organique et de 0,5 à 1% d'un fixateur de radicaux libres ou d'un anti-oxydant.

9. Procédé d'amélioration de la durée de vie en récipient d'un alliage d'au moins un polyamide et d'au moins un polymère d'éthylène contenant des groupes acides carboxyliques, ledit procédé comprenant l'incorporation, dans ledit alliage, d'un composé acide carboxylique organique tel qu'il est défini dans l'une quelconque des revendications 1 à 6.